Renewable and Sustainable Energy Reviews 90 (2018) 557–569

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Natural and synthetic refrigerants, global warming: A review

Naeem Abas[a,*], Ali Raza Kalair[b], Nasrullah Khan[b], Aun Haider[c], Zahid Saleem[d], Muhammad Shoaib Saleem[c]

[a] Department of Electrical Engineering, University of Gujrat, Hafiz Hayat Campus, Gujrat, Pakistan
[b] Department of Electrical Engineering, COMSATS Institute of Information Technology, Islamabad, Pakistan
[c] Department of Electrical Engineering, University of Management and Technology Lahore, Sialkot Campus, Pakistan
[d] Abasyn Universty, Islamabad Campus, Pakistan

ARTICLE INFO

Keywords:
Ozone Depletion Potential (ODP)
Global Warming Potential (GWP)
Natural refrigerants

ABSTRACT

Halogenated hydrocarbons with high ozone depletion potential (ODP) were banned under Montreal Protocol (1987) due to their detrimental effects on ozone layer that shields the planet against ultraviolet radiations. The greenhouse gases (GHG) used in modern refrigeration, air conditioning, and heat pumping systems, are under Kyoto Protocol (1997)'s time-barred permission period. In order to reduce the depletion of ozone and reverse the climate change effects, the European Union legislation (2014) and Paris Accord (2016) are strongly emphasizing the phasing out of the use of harmful synthetic refrigerants. Choice of natural refrigerants makes no net addition of the greenhouse gases (GHG) in the environment. To retrofit and modify existing cooling and heating systems using natural refrigerants, extensive investigations are in progress worldwide. This work reviews timeworn, current and the next-generation refrigerants using Refrigerant Qualitative Parametric (RQP) quantification model to assist the refrigerant choice decision process. It is based on the ratio of arithmetic sums of actual parametric values of refrigerants normalized to equivalent ideal values. This model can help in choosing alternative refrigerants to replace CFCs by HCFCs or HFCs provisionally and finally replacing HCFCs or HFC to low GWP and ODP synthetic and natural refrigerants. A set of 16 refrigerants, both natural and synthetic, as an example, is computed for the standard Vapour Compression Cycle (VCC) based on the proposed model using REFPROP (NIST- 23 standard). The techno-economic parametric values of chosen refrigerants are taken from cited literature, ASHREA safety standards and international environmental legislations, laws and protocols. This paper reports the environment benign natural (CO_2, NH_3, HCs) and a few synthetic (R-152a, R-1234yf) refrigerants to be the optimal options.

1. Introduction

The refrigerant is a substance or mixture, normally a fluid, used in heat cycle undergoing a reversible phase transition from a liquid to a gas and back. Refrigerators, air-conditioners, heat pumps, water heaters and many more devices use refrigerants as a mediating fluid to transfer heat between sources and sinks.

Refrigerants with suitable properties are chosen for selective cooling and heating applications [1]. Human society was using refrigeration technology, even before the invention of electricity in the 1880s. Historically, Oliver Evans (1805) pioneered the idea of refrigeration by using ether,. Jacob Perkin implemented this idea in his first refrigeration machine built in 1834. Later on, various researchers used petrol (1860s), NH_3 (1873), CO_2 (1886) and SO_2 (1890s) as mediating fluids in their refrigeration systems. From 1830 to 1930, ether, NH_3, CO_2, SO_2, H_20, CCl_4, $HCOOCH_3$, HCs, CHCs were the most popular refrigerants. Most of these refrigerants were toxic, flammable, and highly reactive and prone to accidents [2]. Midgley and Henne [3] invented the dichlorodifluorocarbon (CCl_2F_2) molecules in 1929, which were commercially produced as Chlorofluorocarbon (CFC-12) refrigerants by Dupont de Nemours in 1932 [4]. Widespread adoption of efficient CFC refrigerants in 1930s reduced the use of NH_3 and phased out CO_2 by 1950s. CFCs have been used for years as refrigerants, solvents and blowing agents by industry. Long journey of refrigerants from CO_2, NH_3 and HCs to HCFCs, HFCs and HFOs is once again ending up in mix of natural and synthetic refrigerants (CO_2, NH_3, HCs, HFO,R-152a, R-1234yf). There is no refrigerant in sight, which has all ideal properties [5]. A brief history of past, current and probable future natural refrigerants is shown in Fig. 1.

Early refrigeration history (1800) kick started with the use of natural refrigerants, which were replaced by synthetic refrigerants (1929) with superior thermal performance, safety, and durability. Some of the

* Corresponding author.
E-mail address: naeemkalair@uog.edu.pk (N. Abas).

https://doi.org/10.1016/j.rser.2018.03.099
Received 11 August 2016; Received in revised form 28 February 2018; Accepted 31 March 2018
Available online 24 April 2018
1364-0321/

Nomenclature

P_E/p_C Pressure ratio
pr Reduced Pressure = p_{Conds}/p_{crit}
μ (μPa-s) Dynamic Viscosity
h_{fg} (KJ/kg) heat of vaporization
ķ(m-w/m-K Thermal Conductivity
T (°C) Temperature
P (bar) Pressure
C°p (J- mol^{-1} k^{-1}) Specific heat at constant pressure
ρ (kg/m^3) Dynamic Viscosity
p_{reduc} p/p_{crit}, Reduced Pressure
P_r Prandtl no.
p_{Cond}/p_{Evap} pressure ratio
MROA (°C) Maximum Range Of Applicability(T_{max})
M (kg/kmol) Mass of refrigerants
COP Coefficient of Performance
V_{SP}(m^3/kg) Specific Volume
ω Acentric factor
LFL Lower Flammability Limit
p_{Cond}/p_{Evap} pressure ratio
CR Compression ratio p_{Conds}/p_{Evap}

Subscripts

FP Freezing point
NBP Normal boiling point (1.01 bar)
Evap Evaporator
crit Critical
v vapour
n normalized
red Reduced pressure
IG Auto ignition temperature
Conds Condensor
l liquid
a actual

synthetic refrigerants, chlorofluorocarbons (CFCs) were noted to cause stratospheric ozone depletion, therefore, were banned under Montreal Protocol (1987). As a substitute, the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) were proposed in 1980s. HCFCs were noted to cause ozone depletion and bear high global warming potential. Kyoto Protocol (1997) scheduled a phase out of HCFCs by 2020–2030 and HFCs by 2025–2040. Short-term permission to use HFC is an interim solution, not any justification. We are fast approaching the deadline, yet many countries are insolent, reluctant, and unaware or lack financial resources or technical know-how. This work reviews past, present and future outlook of refrigerants and assists the change decision process from high to low GWP and natural refrigerants for existing and future heating as well as cooling machines. An updated review on ozone depletion and global warming is also presented and current status is critically reviewed. Existing refrigerants are simulated for the standard Vapour Compression Cycle (VCC) based on the proposed model using REFPROP (NIST- 23) and original results are presented.

2. Natural refrigerants

Natural refrigerants occur in nature's chemical and biological cycles without human intervention. The natural refrigerants include ammonia (R-717), carbon dioxide (R-744), sulfur dioxide (R-764), water (R-718), air (R728) and ethyl ethers (R-610). Natural refrigerants were heart of HVACR industry from 1800s to 1930s until invention of high performance synthetic refrigerants. Rampant rise in synthetic refrigerants and fossil fuels started causing ozone depletion and global warming, which forced scientific communities and manufacturing industries saying goodbye to halogenated hydrocarbons in favor of natural refrigerants and fossil fuels in favor of sustainable and renewable energy technologies [8,9].

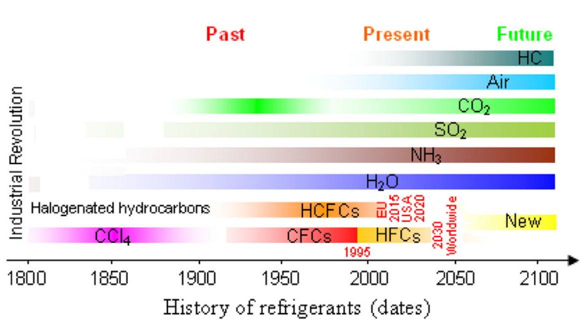


Fig. 1. A brief histogram of synthetic and natural refrigerants [6,7].

2.1. Water (R-718)

Water (R-718) is a non-toxic, non-flammable and abundantly available on planet earth everywhere. R-718 has high refrigeration effect as compared to CFCs, but requires ten times more volumetric flow for a given refrigeration capacity, this enhances the cost in the form of axial or centrifugal compressors [10,11]. Lee incorporated a simulation study using vapour R-718 as a refrigerant in a multi-stage compressor unit with inter-cooling strategy; he articulated that vapour R-718 has 30% higher COP compared to synthetic R-134a at full load. Kilicarslan et al. [12] presented a simulation based comparison between R-718 with R-290, R-717, R-134a, R-22 and R-152a for an evaporation temperature above 35 °C, and found R-718 exhibiting higher COP. Thermophysical properties of R-718 allow achieving COP, however, its high critical temperature (373.95 °C) and pressure (221 bar), high initial cost of axial or centrifugal compressors, high volumetric flow, large compression process, use of direct contact heat exchangers are limiting factors, rendering R-718 less attractive for heat pump applications [13].

2.2. Hydrocarbons (HCs)

Hydrocarbon (HCs) refrigerants include methane (R-50), ethane (R-170), propane (R-290), butane (R-600), isobutene (R-600a), ethylene (R-1150) and propylene (R-1270). HCs are ozone friendly and have a lower GWP as compared to HFCs. HCs offers excellent miscibility with synthetic oil, lower refrigerant charge and are compatible with the material of existing refrigeration and heat pump systems. Methane (R-50) and Ethane (R-170) are a flammable cryogenic liquid has an extremely low boiling point of − 162 °C and − 88.58 °C, respectively. These are used for extreme low temperature refrigeration (−80 °C). HCs such as propane appear, excellent candidates, to which researchers in contact with industry have reported safety issues [14]. R-290 and R-600 have similar characteristics as halogenated HCs but are flammable materials. R-290 has a higher cooling capacity than R-12 and similar COP when tested in propriety vapour compression refrigeration system [3]. The similar results were presented by B. Saleh and his fellow researchers using BACKBONE equation. R-1270 is an effective alternative of R-22 with higher capacity and COP [15,16]. Ignition temperatures of HCs are in the range of 420 °C (R-600) [17] to 600 °C (R-50) [18]. HCs have excellent environment friendly thermodynamic properties, but they are flammable. According to Missenden et al., a restricted amount of 200 g of HC refrigerant is recommended for domestic refrigeration systems whereas this amount does not exceed 0.40 g in such systems [19]. However Corberan et al. refereed to an amount of 150 g form a small sealed system in accordance with ISO, EU, IEC standards [16].

When some of the hydrogen atoms are replaced by chlorine, fluorine and bromine the flammability reduces but start churning out undesirable environmental effects which do not let them anymore natural refrigerants.

HCs refrigerants are used in domestic refrigerators, freezers and air-conditioners. Commercial applications include beverage, ice-cream machines, truck mounted refrigerators, heat pumps and 0.3 (1 kW) to 40 (150 kW) ton chillers [20]. Domestic refrigerators may use R-290 and R-600a; commercial medium temperature equipment may use above as well R-170 (for sealed hermetic) for low temperature applications. R-600a is extensively used as refrigerant in domestic refrigeration units in Europe and other parts of the world [21]. With growing large commercial and industrial compressors may use R-170, R-290 and R-600a. Air conditioners may use R-600a for centrifugal or hermetic and R-600a, R-290 [22]. A mixture of R-290 and R-600a (50%, 50%) performs better refrigeration when compared with R-134a saving up energy by 4.4% with a reduced refrigerant amount [23].

2.3. Air (R-729)

Air (R-279) is an environment benign refrigerant, having zero ODP and GWP with a broad range of temperature applicability (−213.15°C to 1726.85 °C). Air has low critical pressure of 37.2 bar but extremely low critical temperature of − 140.32 °C. R-729 is used in aircraft, high speed train air-conditioning, and industrial ultra-low temperature refrigeration system (−50 °C to −100 °C) [24,25]. Miller et al. [26] patented the basic idea of Compressed Cycle Air Refrigeration (CCAR) in 1996 using R-729 as refrigerant [26]. R-729 is effectively used in open cycle, closed cycle and semi-open/closed cycle refrigeration using reverse Brayton cycle. The low COP, high cost, and large system size are potential challenges using R-729 as mediating fluid [27].

2.4. Ammonia (R-717)

Ammonia (R-717) and has been used as refrigerants for refrigeration and air-conditioning for several decades before the invention of electricity. The R-717 has zero ODP and GWP, excellent thermodynamic properties and high heat transfer coefficient. R-717 has widespread use in medium and large food, beverage and preservation industry. Many authors have proposed its potential use in low capacity heat pump applications but has not received wide spread acceptance [28]. In vapour phase, R-717 gas is lighter than air and easily mixes in water. Its lower explosion limit is 15% and ignition temperature is 651 °C. Ammonia has lowest molar mass among all natural and available synthetic refrigerants making its compressor to have lower swept volume. R-717 has a high latent heat of vaporization (1313.2 KJ/kg), critical temperature (132.25 °C) and pressure (113.33 bar) seems favorable in terms of COP for VCC compared to CFCs and HFCs. Prof. Palm [29] employed ammonia in domestic heat pump (9 kW) water heating successfully with a COP of 3.8–4.8. It is a self-alarming gas as ammonia leakage is easily detected by its smell even at 5 ppm concentration. Although, ammonia threshold limit value is 25 ppm it becomes fatal only beyond 5000 ppm. It has lower flammability in air when its concentration is between 16% and 28% by weight. However, ammonia is not compatible with copper, zinc and copper alloys which render it to legal regulations and standards for personnel safety [30]. Water and ammonia corrosive nature render them incapable to replace the existing copper tubes networks. The use of ammonia as refrigerant is restricted in residential and commercial systems. A semi-hermetic design may be the way out through secondary cascade. However, its poor miscibility requires a separate mechanism for oil return to the compressor. Ammonia, despite of having flammable, toxic and reactive hazards are still famous for last 100 years in the food industry. However, in low capacity heat pump applications the system components, safety hazards are major challenges.

2.5. Carbon dioxide (R-744)

Carbon dioxide (CO_2) is an old natural refrigerant having zero ODP and lowest effective GWP. It is heavier than air, non-toxic, non-flammable, abundantly available in the air and a by product of many industrial applications. Before 1950, it was used in marine applications later replaced with synthetic refrigerants due to its lower operating pressures. R-744 is inexpensive, exhibits low liquid density results in lower system size and charge quantity. Modern refrigeration and air-conditioning requirements demand lowest boiling point, high critical temperature and moderate critical pressure refrigerants [31]. R-744 has over 5.8 times higher refrigeration capacity at very low critical temperature. Trans-critical property of CO_2 desires supercritical pressure for heat rejection. It is being used in trans-critical regime in most refrigeration and heating applications. The high pressure, low molar mass of CO_2 reduce volumetric flow and dimensions of system components. Production and transportation of CO_2 has carbon equivalent of 1 kg CO_2 $_{eq}$ per kg, whereas NH_3 and HFC have equivalent carbon of 2 and 9 kg CO_{2eq} per kg.

CO_2 (R-744) has replaced glycols, and salt brines as a secondary refrigerant. When CO_2 is used as refrigerant in supermarkets the coefficient of performance for 90% of the year is higher than HFC based systems. Lorentzen patented the idea of transcritical CO_2 auto-motive air conditioning [32] and now being used as a refrigerant in air-conditioning in the transportation system. It works at ten times higher pressure compared ammonia requiring especial equipment but it offers high gas density allowing greater refrigerating effect. R744 (CO_2) offers a high refrigeration capacity of 22,600 kJ/kg at 0 °C which is 5–22 times higher than other synthetic and natural refrigerants. CO_2 produces small reductions in saturation temperature for pressure drop allowing higher mass flux in evaporator and suction pipes. This effect becomes noticeable at − 30 to − 50 °C where higher efficiencies have been reported. It is equally popular for low temperature freezers as well as high temperature heat pumps. When CO_2 pressure exceeds 73.8 bar it is not possible to condense the gas without temperature glide.

Authors have designed, fabricated and tested CO_2 based gravity

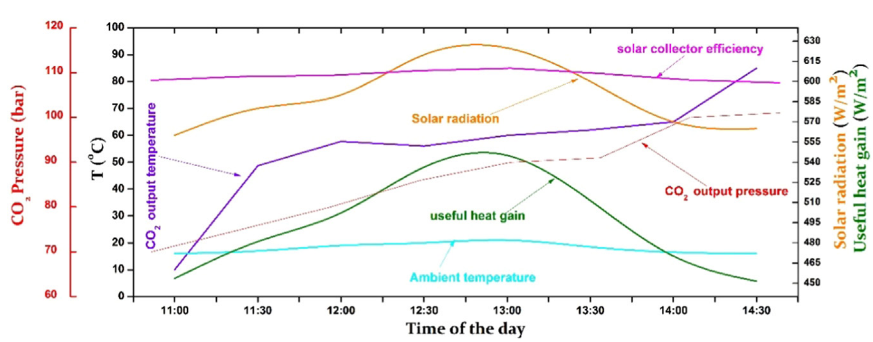


Fig. 2. Experimental results of CO_2 based density driven system [36].

driven solar water heater that can outperform in even subzero temperature with extremely low solar insolation regions like Gilgit in Pakistan and Fargo in the USA [9,33–35]. After some design modifications and increasing the working pressure the proposed system demonstrated efficiency of 82% even in mild sunshine as shown in Fig. 2. [36].

In our preceding work, authors demonstrated that supercritical CO_2 as optimum refrigerant among ASHREA envisaged natural refrigerants in the working temperature range − 20 to 30 °C and 30–70 °C for thermo-syphon driven solar water heaters [37].

2.6. H_2 (R-702)

H_2 (R-702) has low critical pressure (13 bar) but the extremely low critical temperature (−239.95 °C). Helium (R-704) has a relatively higher critical temperature (4 °C) than air and hydrogen, but it has an extremely low critical pressure (−268.93 bar). Methane (R-50) and Air (R-729) exhibits sub-zero critical temperature and boiling point, respectively. Ethylene (R-1150) has a very low critical temperature (9.2 °C), while water has frozen point at 0 °C, which make these refrigerants not appropriate for normal refrigeration cycle and thus not included in this study. Apart from high critical temperature and low pressure other parameters like toxicity, flammability and refrigeration capacity have to be considered before a final choice. The characteristics of some natural refrigerants are shown in Table 1 [1,4].

Among the cluster of selected natural refrigerants, all exhibit fairly low enough freezing point (−59 to −188 °C) and normal boiling point except R-600 (−0.49 °C) and R-600a (−11.75 °C). HCs have lower reduced pressures and heat transfer in boiling phase, except R-170, which result in inferior thermal performance. The vapour pressure curve of selected natural refrigerants is shown in Fig. 3.

All refrigerants exhibit fairly low enough freezing point (−59 to −188 °C) and normal boiling point temperatures, except R-600 (−0.49 °C) and R-600a (−11.75 °C). R-170 has optimal lower pressure ratio among all chosen refrigerants whereas other HCs show a nominal trend. This substantially explains higher isentropic and volumetric efficiency of R-170 over other refrigerants.

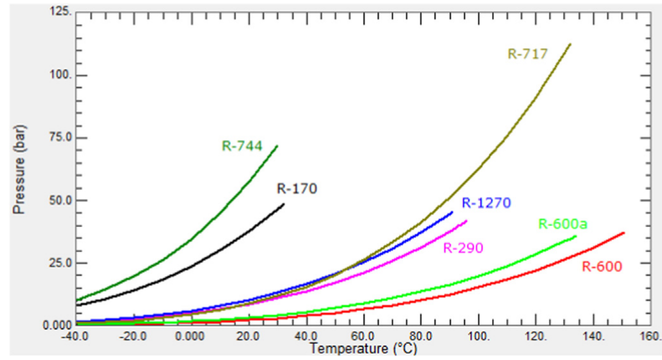


Fig. 3. Critical temperatures and pressures of some natural refrigerants.

3. Synthetic refrigerants

Discovery of CFCs and HCFs accelerated the industrial growth and human comforts at the expense of ozone depletion and climate change. Regular synthetic refrigerants from 1930 to 2000, HFC (R-134a, R-32, R-125, R-143a, R-152a), HCFC (R-22, R-141a, R-141b, R-123), PFCR-14), PCC (R-110), HFO (R-1132). CFCs (R-12 and R-114), were replaced easily by HCFC (R-134a) and HCFs, but some of CFC refrigerants such as R-11, used as a solvent and blowing agent, could not find alternatives. HFCs do not cause global warming; however, when it is exposed to UV in the troposphere, it may decompose to form an acid and poisonous substances, which rain down sooner or later. Large scale use

Table 1
Standard parameters of some ASHREA envisaged future natural refrigerants [1,4].

	Groups	Natural Refrigerants						
Type	Parameters	(R-170)	(R-290)	(R-600)	(R-600a)	(R-1270)	(R-717)	(R-744)
Environment	ODP[1]	0	0	0	0	0	0	0
	$GWP_{(100\text{-}Years)2}$	20	20	20	20	20	0	1
	Life (Yrs)	12	12	12	12	12	0.019	1
	MROA (°C)	401.8	376.8	301.8	301.85	301.85	426.85	1726.9
Physical	T_{FP}(°C)	−183	−188	−140	−159.6	−59	−77.73	−78
	T_{NBP}(°C)	−88.58	−42.11	−0.49	−11.75	−47.62	−33.33	−78.46
	T_{CP}(°C)	32.17	96.74	151.98	134.66	91.06	132.25	31.1
	T_{IG} (°C)	505	470	420	460	460	850	∞
	P_{Evap}[3](bar)	16.29	2.916	0.563	0.890	3.6302	2.3617	22.908
	P_{Conds}[4](bar)	46.55	10.790	2.834	4.0472	13.050	11.672	72.137
	P_{crit}(bar)	48.72	42.512	37.96	36.29	45.55	113.33	73.77
	$h_{fg\ evap}$(kJ/kg)	350.6	394.65	398.23	367.97	399.09	1313.2	270.93
	V_{SPevap}[5](m^3/kg)	0.0334	0.1538	0.6375	0.39904	0.12815	0.50868	0.01646
Transport Properties at 30 °C	μ_l (μPa-s)	292.42	92.188	151.07	143.43	91.479	125.45	43.768
	μ_v (μPa-s)	8.15	8.4628	7.5182	7.6308	9.1707	9.9953	25.170
	k_l (m-w/m-K)	153.12	91.409	102.66	87.489	110.14	471.35	95.356
	k_v(m-w/m-K)	14.561	19.724	17.114	17.371	19.722	26.846	98.023
	h_{fg} (kJ/kg)	529.10	326.70	356.30	323.33	324.98	1144.4	60.575
	ρ_l (kg/m^3)	779.02	484.39	566.98	544.31	497.45	595.17	593.31
	ρ_v (kg/m^3)	0.900	23.451	7.1366	10.480	27.718	9.0533	345.10
	p_{reduc}	0.955	0.253	0.074	0.111	0.286	0.103	0.978
Performance properties	C°p (298 K)	52.456	73.307	98.442	96.598	64.376	35.637	37.134
	(J- mol^{-1} k^{-1})	30.069	44.096	58.122	58.122	42.08	17.03	44.01
	M (kg/kmol)	2.85	3.70	5.033	4.54	3.59	4.94	3.14
	CRω	0.0995	0.1521	0.201	0.184	0.146	0.2560	0.22394
Chemical	ASHREA-34	A3	A3	A3	A3	A3	B2L	A1
	Miscibility	Y[6]	Y[6]	Y[6]	Y[6]	Y[6]	N	N
	Reactivity	No	No	No	No	No	Yes	No
Fiscal	Cost/kg in $ (in Pakistan)	1.5	1.3	3.1	2.0	3.1	1.5	0.7
	Availability	Y	Y	Y	Y	Y	Y	Y

of HFCs may cause another catastrophe, like fossil fuels electricity driven electric cars, which might be even worse than CFCs [7]. After the ban on CFC (R-12) production in 1995 the HCFC (R-22), HFC (R-134a), PFC (R-14), PCC (R-110), HFO (R-1132a) and HFO (R-1132a) were timely permitted for a few decades to retrofit the widespread systems to low GWP synthetic and natural refrigerants. Retrofitting of refrigerant requires consideration of several economic and technical aspects for correct decisions.

Mclinden [38] and his co-researchers performed a screening study from 56,000 small molecules and identified a set of 1200 low GWP refrigerants by applying an evolutionary algorithm. Low GWP ($\leq$ 200), none or low-flammability (LFL$\leq$ 0.10 kg/m^2), chemical stability (copper and stainless steel), non-toxicity (human, animal), suitable critical temperature (26.85–126.85 °C), as screening parameters, the refrigerants were pared down to 62 potential candidates. These molecules include halogenated alkenes, fluorinated olefins, halogenated olefins, halogenated oxygenate, halogenated nitrogen, sulfur compound, inorganic and some other compounds. The olefins consist of industry focused hydrofluoroolefins (HFOs) with low values of (GWP < 10). Two commercialized HFOs (R-1234yf, R-1234ze (E) are of modern interest under extensive investigation and research [39]. Halogenated olefins consisting of fluorine plus chlorine or bromine typically having non-zero ODP and low thermodynamic cycle efficiency [38]. Halogenated oxygenates are of less interest in future due to their environmental degradation property (Carbon-carbon double bond). Halogenated nitrogen compounds have higher values of GWP (11 − 64) and possess low thermodynamic properties [40]. Sulfur containing compounds is problematic due to material compatibility. Inorganic compounds (NH3, CO_2) will be future interest refrigerants. Characteristic parameters of some synthetic refrigerants are shown in Table 2.

Mohanraj et al. comprehensively reviewed the alternatives of halogenated refrigerants and suggested use of hydrocarbons (HCs) and Hydroflourocarbons (HFCs) and their mixtures as future alternate of existing refrigerants [44]. Babiloni et. al propose synthetic refrigerant HFOs (R1234yf, R1234ze (E &Z) and R152a as alternative to HFCs in new HVACR systems [45,46]. Historically, different authors performed theoretical, empirical and experimental studies and suggested various alternatives of environmental perilous refrigerants. Table 3 shows a brief history of some of these works.

The refrigerant industry is exploring new avenues to meet future refrigeration and air-conditioning needs. Heat pump systems often require moderate critical pressure and high critical temperatures for optimal heat transfer. A plot of critical temperatures and pressures for commonly used synthetic refrigerants is shown in Fig. 4.

From Fig. 4, it is evident that R-1234yf have similar vapour pressure curve like R-12 and R-134a showing their effective alternative [65]. R-143a exhibits lower pressure ratio (p_{Conds}/p_{Evap}) but has a high GWP (353). R-1234ze and R-134a have higher pressure ratios and consequently lower isentropic and volumetric efficiencies [66]. Coefficient of Performance (COP) of simple and extended VCC is highly dependent on critical temperature, higher the value, increasing trend in COP is noted [40] R-152a and R-1234ze are prominent among the cluster, whilst other refrigerants such as R-134a, R-12, R-22, R-1234yf shows them standing above 90 °C.

4. Ozone depletion and global warming: twin challenges

John Tyndall affirmed water vapors, CO_2, and ozone as atmospheric heat absorbers in 1861. John feared shortage of any of them might cause global cooling, and Swante August Arrhenius alarmed possibility of global warming due to rampant amount of CO_2 emission in 1896 [67]. Charles started measuring the concentration of CO2 in the atmosphere in 1955. Molina and Rowland in 1974 explained how CFC molecules destroy ozone in the stratosphere [68]. British scientists

Table 2
Standard techno-economic parameters of synthetic refrigerants [17,38,41–43].

	Groups	Synthetic Refrigerants								
Type	Parameters	R-12	R-22	R-32	R-125	R-143a	R-134a	R-152a	R-1234yf	R-1234ze(E)
Environment	ODP [1]	1	0.05	0	0	0	0	0	0	0
	GWP [2] $_{(100\text{-Years})}$	8100	1810	675	3500	4470	1430	124	4.0	6.0
	Life (Yrs)	100	12	4.9	29	52	14	1.4	0.03	0.05
	MROA (°C)	251.8	267.85	161.8	226.8	376.8	181.8	226.8	136.8	146.8
Physical Properties	T_{FP}(°C)	− 157.5	− 160	− 137	− 103	− 111	− 97	− 111.3	− 150	− 150
	T_{NBP}(°C)	− 29.5	− 41	− 51.65	− 48.09	− 47.24	− 26.07	− 24.02	− 29.45	− 18.95
	T_{CP}(°C)	111.97	96.15	78.11	66.02	72.71	6.06	113.26	94.7	109.37
	T_{IG} (°C)	757	630	708	760	660	739.95	455	404.85	368
	P_{Evap} [3](bar)	1.82	2.96	4.88	4.05	3.77	1.63	1.48	1.83	1.20
	P_{Conds}(bar)	7.45	11.91	19.27	15.68	14.34	7.70	6.89	7.83	5.78
	P_{crit}(bar)	41.3	49.9	57.8	36.1	37.6	40.5	45.1	33.8	36.3
	$h_{fg\ evap}$(kJ/kg)	159	216.4	337.28	144.07	201.7	209.5	321.71	172.3	193.1
	$V_{SP}\ ^{5}_{evap}(m^3/kg)^5$	0.091	0.0775	0.0749	0.03923	0.0598	0.1206	0.2064	0.09527	0.1492
Transport Properties at 30 °C	$\mu_{l\ (\mu Pa\text{-}s)}$	178.8	155.4	107.2	130.0	108.3	183.1	153.8	146.5	188.0
	$\mu_{v\ (\mu Pa\text{-}s)}$	11.85	12.77	13.12	13.91	11.48	11.90	10.25	12.55	12.45
	k_l (m-w/m-K)	65.3	81.20	122.10	57.38	68.38	78.99	95.85	62.03	72.67
	k_v (m-w/m-K)	10.6	11.80	16.03	16.20	17.49	14.33	15.411	14.478	14.05
	$h_{fg\ l\ (KJ/Kg)}$	136.2	177.64	260.4	104.8	152.5	173.10	273.16	141.24	162.9
	ρ_l (kg/m^3)	1292.7	1170.7	939.6	1158.4	908.45	1187.5	886.61	1073.3	1146.3
	ρ_v (kg/m^3)	42.06	50.70	54.77	105.1	66.605	37.53	21.35	43.72	30.56
	p_{reduc}	0.18	0.238	0.333	0.434	0.381	0.190	0.152	0.231	0.159
Performance properties	C°p (298 K)	74.00	56.15	42.93	94.40	78.05	85.00	66.50	101.50	99.30
	(J- mol^{-1} k^{-1})	120.91	86.47	52.024	120.02	84.041	102.03	66.051	114.04	114.04
	M	4.09	4.02	3.94	3.87	3.80	4.72	4.65	4.27	4.81
	(kg/kmol) CR	0.179	0.220	0.277	0.305	0.261	0.327	0.275	0.276	0.313
	ω									
Chemical properties	ASHREA-34	A1	A1	A2L	A1	A2L	A1	A2	A2L	A2L
	Miscibility	Y	Y[6]	Y	Y	Y	Y	Y	Y	Y
	Reactivity	N	N	Y[8]	N	N	N	N	N	N
Fiscal properties	Cost/kg in $	7	11	3	2.5	3.3	5.3	1.5	88	90
	(in Pakistan)	Y	Y	Y	Y	Y	Y	Y	Y	Y
	Availability									

Table 3
Historical outlook of halogenated refrigerant and their proposed alternatives.

Year	Refrigerant	Alternative	Conclusions & Suggestions	Source
1990	R-11, R-12, R-113, R-114	E-134, E-123b, E-143,C236	Proposed new compound HCFC as replacement of CFC in lieu of environmental legislation.	[47]
1992	CFC12	HFC134a and HFC152a	Author performed theoretical performance evaluation of refrigerants by selecting pressure ratio, specific compressor displacement, theoretical Rankine coefficient of performance, shaft power per ton as parameters. Results proposed that HFC134a and HFC152a work closer by performance to CFC12.	[48]
1993	R152a	R32a	Author analyzed vapour pressures and coexisting densities of refrigerants R-32 and R-152a through experimental measurements from 300 K to near their individual critical points. Critical density points for R32a are found higher values as compared with R152a.	[49]
1994	R134a and R124	R22	Author measured density and vapour pressure of R22, R134a, and R124. Results of compressed densities of R22 were found as per literature, while divergence was noticed for R134a and R124.	[50]
1994	CFC / HCFC	NH_3, C_3H_8, CO_2	CFC and HCFC are foreign to nature and are dangerous. The author proposed use of natural refrigerants at the cost of change in design and practice of equipment.	[51]
1996	CFC	HFC23 and HFC32	Liquid simulations of alternative refrigerants HFC-32 and HFC-23 have been performed to observe their effective potentials. The calculated PVT properties and heat of vaporization are found in the reasonable limit as per literature, and simulated heat of vaporization for HFC-23 is found steadily about 9% larger than the experimental values.	[52]
1997	CFC	R134a and R125	Paper presents vapour-liquid equilibrium (VLE) for six binary mixtures of the new hydrofluorocarbon refrigerants. From samples, R134a and R125 presented close results to expected values.	[53]
1998	CFC	R123, R124, R125, R134a, R143a, R152a, R218, and R236ea	This study describes alternative refrigerants with BACKONE equations. Results are satisfactory in accordance with reference Helmholtz function (RHF).	[54]
1999	R-12	Ratios of propane, butane, and isobutane	An experimental study to find the performance of ratios of propane, butane and isobutene to the traditional R-12 refrigerant in a domestic application. Results are satisfactory with different ratios of these three refrigerants instead of single.	[55]
2000	R22	Blend of R-32/R-134a in 20 ± 80%	Author studied thermodynamic properties of blends of R-32/R-134a in 20 ± 80% ratios. COP values are found reasonable to replace R22 in results.	[56]
2001	CFC	R12, R134a	In this study, a model for R12 and R134a has been compared with experimental data. Conventional refrigerants show lower pressure drops.	[57]
2005	HFC-161	R502	A near-azeotropic mixture of HFC-161 as the alternative refrigerant of R502 having zero ODP and Lower GWP is presented in study and according to results, it can attain high COP.	[58]
2007	R-22	Mix of (R1270), propane (R290), HFC152a	Author studied thermodynamic performance to replace HCFC22 with mixtures of (R1270), propane (R290), HFC152a in residential air-conditioners. Results showed handsome environmental benefits with these new blends and amount of charge was decreased up to 55% as compared to R-22	[59]
2009	R-134a	R430A	The experimental and numerical analysis is performed to replace HFC134a by R430A in household water purifiers. Results suggest it as a good alternate without any change in the system.	[60]
2011	R-22	R404A and R507	An experimental study was performed to investigate R404A and R507 as alternatives of R22 in window air-conditioner. R507 was found best alternative according to results of COP and refrigeration capacity.	[61]
2015	CFC/HCFC/HFC	R-1234yf, R-1234ze(Z), R-1216, R-1233zd(Z), R-1233zd(E)	This research group suggested short-chain haloolefins as replacement of saturated hydrocarbons with negligible GWP and zero ODP.	[62]
2016	R22	R-1270 and R-290	Experimental investigation of a 5-ton refrigeration system to replace R22 with alternative natural refrigerants is performed. Results opted R1270 as best option having high COP, lower GWP, and reduced carbon taxes.	[63]
2016	HFOs	R1234ze (E)	Authors recommended to use R1234ze(E) in new HVACR systems.	[45]
2017	Halogenated	R-290 to replace R-22 HCs and mixtures to replace R-12 and R-134a	The author provided an updated review of existing literature with recommendations to use natural refrigerants and their mixtures as an alternative of halogenated.	[64]
2018	HFOs	R152a, R1234yf and R1234ze(Z)	The authors discussed future refrigerants suitable for replacing the traditional HFCs	[46]

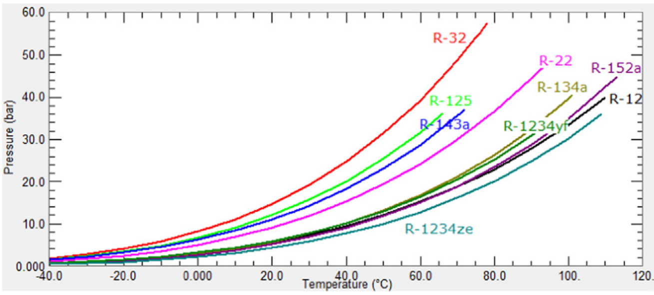


Fig. 4. Critical temperatures and pressures of Synthetic refrigerants.

noted a hole in the ozone layer in Antarctica in 1985. French and Soviet scientists analyzed Antarctica ice core to show a close correlation between CO2 concentrations and temperatures in previous 100,000. Geologists hold the CO2 level in the atmosphere increased to 3000–3500 ppm (8–10 times higher than today) some 55–65 million years ago due to escape of hydrate gas from deep oceans [69]. Deep sea tsunamis can rehearse the event anytime as the marine gas hydrates reserves are reported to be twice of our all coal, oil and gas reserves. Scientists are fearing the return of Ice Age started worrying about the return of great inferno due to global warming for rising combustion rates of fossil fuels. Current annual global energy consumption in the forms of food (6.97PWh), electricity (24PWh) and fuels (116PWh) is 147PWh, which at an average efficiency of 30% equals to 490PWh input energy.

The environmental ranking of refrigerants, using Hasse diagram technique, is reported in the literature [70]. It is a mathematical method to assess the relationship between various chemicals. This ranking has been done using upon ozone depletion potential, global warming potential and atmospheric lifetime. It has been found that hydrocarbons and ammonia are the least problematic with respect to above three properties. The cycle performance of 39 Air-Conditioning, Heating, and Refrigeration Institute (AHRI) low GWP refrigerants in a typical air conditioner has been reported in [70]. Each refrigerant has been evaluated under same evaporator heat duty and temperatures of sink. The top three refrigerants are identified as R1234yf, R32, and R1270. The life of most green gases is less than one century, but some of them stay in the atmosphere for several thousands of years. The even strict following of phase out deadlines, already emitted CFC would be responsible for 4–10% of halocarbon based total global warming [71].

Awareness on ozone depletion and global warming eventually led to the Montreal protocol in 1987 [72] and Kyoto Protocol in 1997 [73], respectively. World leaders meet periodically to monitor the compliance and discuss future strategies. Ozone is a poisonous gas located upto eleven kilometers above the surface level. It is composed of three oxygen atoms and shields the earth from harmful solar radiations. The ultra-short wavelengths UVC (100–280 nm) are obstructed by ozone and dioxygen layers. The UVB (290–315 nm) are filtered out by the ozone layer, whereas UVA (315–400 nm) pass through the ozone layer. In case of a hole in ozone layer, the UVB passed through and reaches the surface of the earth causing damages to humans (malignant melanoma, cataracts), plants (growth, secondary metabolism), marine ecosystem (fish, shrimp, crab, phytoplankton), biogeochemical (GHG gases doubling) and materials (polymers) [74]. Ozone Depletion Potential (ODP) of a chemical is the relative amount of degradation to the ozone layer around the earth, compared to R-11 (OPD = 1).

$$\mathrm{ODP} = \frac{\mathrm{Global}\Delta \quad \mathrm{O_3 due\ to\ x}}{\mathrm{Global}\Delta \quad \mathrm{O_3 due\ to\ CFC} - 11} \tag{1}$$

CFCs and HCFCs bear stable chemical bonds, therefore, they can penetrate into the heart of stratosphere, where chlorine reacts with ozone to thin its shield around the earth. Natural chlorine sources such as ocean spray and methyl chloride also deplete ozone, but their contribution is less than 20% compared to over 80% by man-made synthetic refrigerants. ODP of the most CFCs is 1 except CFC-113 and CFC-115, which have 0.8 and 0.6 respectively. OPD standard is based on R-11 or 12, but OPD values for brominated substances vary from 5 to15, i.e. more dangerous than others. ODP for halon-1301 is 10 and R-12B1 is 7.1. ODP for HCFCs are in the range of 0.005–0.2 due to hydrogen bonding, and that of HFCs is 0. HCFCs and HFCs are mostly trapped in the troposphere, but CFCs due to their strong X-C bond can penetrate into the heart (stratosphere) of the zone where one chlorine atom can destroy 100,000 ozone molecules. CFCs have been banned, but their nuisance will continue to exist for years due to their long lives.

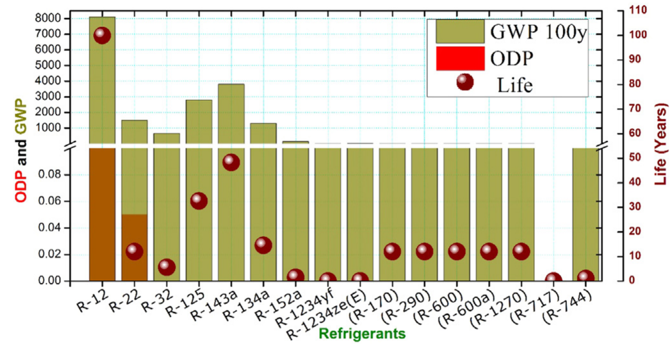


Fig. 5. ODO and $GWP_{100Years}$ plot of common synthetic and natural refrigerants [22,77,78].

Sekiya et al. experimentally showed that nuisance of GHG would continue even after their atmospheric life. The authors introduced Total Warming Prediction Analysis (TWPA) and Composite Warming Potential (CWP). The TWPA can be expressed in quantity (kg) and concentration (W/m^2) which shows the amount of refrigerant or CO_2 in atmosphere responsible for warming [75]. Standard methods are available to measure the rate of reactions of chlorine atoms in the atmosphere to determine their life [76]. Total $GWP_{100Years}$,ODP and atmospheric life time of some regular refrigerants are shown in Fig. 5.

ODP decreases from CFCs to HCFCs, HFCS and HCs, but their GWP increases. After the ban on CFCs global average ozone hole area in the southern hemisphere peaked at 26.6 km^2 in 2006, but declined to 20.9 km^2 in 2014 (F-Gas 2015).

GWP is a relative measure of how much heat a green gas traps in the atmosphere. Sun is the ultimate source that powers the planet by its radiations. More than 30% of solar radiations are reflected back, whereas the rest pass through the atmosphere and reach the surface of the earth. After absorbing solar radiations the earth's surface acts as a blackbody emitting infrared radiations back to the atmosphere. Due to the presence of greenhouse gases like CO_2, CH_4, N_2O and halogenated refrigerant (CFC, HCFC, HFC) they are trapped and thus cannot pass through the atmosphere [79]. GWP depends on the spectral absorption of infrared and life of green gas in the air. Its expression is given by [70].

$$\mathrm{GWP} = \frac{\int_0^\infty f_i(t)C_i(t)dt}{\int_0^\infty f_c(t)C_c(t)dt} \tag{2}$$

Ci(t) is concentration of gas *i* at time t following the emission of a unit amount at time *t = 0*, *fi(t)* is the heat trapping ability at the same time per unit of concentration, and *Cc(t)* and *fc(t)* the corresponding quantities of CO_2 which are expressed as;

$$\mathrm{C_c(t)} = \sum_{i=0}^{4} \mathrm{A}_i \quad \exp\left(-\frac{t}{\tau_i}\right) \tag{3}$$

$$\mathrm{C_c(t)} = A_0 + \sum_{i=1}^{4} \mathrm{A}_i \quad \exp\left(-\frac{t}{\tau_i}\right) \tag{4}$$

The Inter-governmental Policy Panel on Climatic Change (IPCC) has adopted the following definition:

$$\mathrm{GWP} = \frac{\int_0^T f_i(t) C_i(t) dt}{\int_0^T f_c(t) C_c(t) dt} \tag{5}$$

For a mix of GHG, the effective CO_2 emission factor is defined has been defined as follows:

$$F_{eff} = E(F_{CO_2} + \sum F_i GWP_i) \tag{6}$$

Whereas E is fossil fuel consumption (GJ) at the point of use, FCO_2 is CO_2 emission factor (kg/GJ), *Fi* and *GWPi* are fuel consumption and GWP of other emitted gases. FCO_2 for coal, oil and natural gas are 88–95 kg/GJ, 68–73 kg/GJ and 49.5 kg/GJ respectively. The CO_2 level in the atmosphere is still increasing exponentially with a recent value of 409.65 ppm [80] and annual CO_2 emission would increase to 75 Gigatons [37]. The CO_2 concentration and average minimum ozone level and hole area from the year 1979–2016 is plotted in Fig. 6.

Some of high ODP refrigerants such as R-14, R-116, R-218 and R-502 have long lives of 50,000, 10,000, 2600 and 876 years and still used in semiconductor, electronics and commercial refrigeration applications. PFCs like R-4-1-12, R-C318, R-3-1-10 and R-5-1-14 have zero OPD, 9160, 10,300, 8860 and 9300 per 100 year GWP. ODP and GWP of HCFC (R-22) are 18 and 9 times lesser than CFC (R-12) due to the presence of hydrogen bond, so they were allowed for a couple of decades until suitable alternatives are found. CFCs and HCFCs bear stable chemical bonds, therefore, they can penetrate into the heart of stratosphere where chlorine reacts with ozone to thin its shield around the earth. HFC does not deplete ozone but causes global warming; therefore it was permitted for longer periods up to 2030. Montreal Protocol passed a ban on the production of R-12 in 1996 and a scheduled phase out of HFC-22, HFC-141b, HCFC-142b and HCFC-123 with a timeline of 2030 for devolved countries and 2040 by developing countries. Interim substitution of HCFC-22 accelerated its concentration in the atmosphere significantly with an expected doubling effect in 2015 [83,84]. However, in 2007, IPCC rescheduled phase-out of HCFC by 2020 for developed countries and 2030 for developing countries [85,86]. After results of global efforts, the production of CFC-12 declined from 450,000 in 1998 to 230,000 metric tons in 1992. HFC production was also accelerated to meet the replacement needs. According to the latest report on health of ozone layer, the concentration of ozone depleting substances (ODS) are way to major decrease as collective efforts under Montreal Protocol, however, HCFCs and halon-1301 are increasing continuously. Current emission of HFCs (0.5 Gt CO_2-eq) as a replacement to CFC is growing at a steady rate of 7% per year is projected to 8.8 Gt CO_2-eq by 2050 [87].

Climate change drives the hurricanes, cold and heat waves. Hurricane Harvey, Irma and Maria inflicted zillions of dollars loss in USA, Cuba and Puerto Rico last month. Extreme weather events warn us all to move towards environmental benign fuels and refrigerants. To slow down the climate change process, we have to reduce GHG emissions, population growth, consumption of fossil fuels and comforts [88]. Driving an air conditioned car, remember it is heating the planet. Rampant rise in fossil fuel consumption pollutes air and increases GHG emissions. Energy thrives on energy as money begets money. High energy consumptions produce more GHG emissions as higher investments earn more profits [89]. Population growth, economic booms and high energy consumptions are the drivers of climate change inflicting cold and heat waves. We have emitted 1540 billion tons of CO_2 in the atmosphere - deducting forests and ocean uptake − 850 billion tons CO_2 is present in the atmosphere. Cold and heat waves are integral part of natural weather. Recent climate change phenomenon has increased frequencies, intensities and durations of cold and heat waves. To live in harmony with natural worldlet the sun shine, winds waft, forests foster and earth breathe. Let the nature speak, which is whispering to abandon fossil fuels and synthetic refrigerants. Heat, light and electricity are three forms of energy. Combined heat and power (CHP) is more economic than single heating or power production. Solar energy provides light, heat and electricity. CHP systems may incorporate cooling too. Solar energy is ideal for heating and heat or electricity driven cooling. intermittent solar and wind energy sources facilitate CHP system [90,91]. Solar heating and cooling system using borehole thermal energy storage and nano-fluids offers an integrated efficient energy system [92,93]. Application of nano technology in natural refrigerants and adoption of combined heating, cooling and power (CHCP) is more sustainable solution than separate or combined heat and power systems.

5. Qualitative parametric quantification

The choice of a refrigerant for heat transfer depends on a wide range of technical, environmental, chemical, economic and legal considerations. Several techno-economic and environmental issues restrict choosing well known optimal performance refrigerants. A refrigerant may be suitable for refrigeration or air-conditioning but may not be good for heating applications. The refrigerants should have a minimum pressure drop, which can be achieved by its thermo-physical characteristics, i.e. the lower viscosity, high density and heat of vaporization [94]. According to cooper's pool boiling correlation, the refrigerants offering high reduced pressure and lower molar mass result in high heat transfer in boiling [95,96]. However, at condensation, high density, thermal conductivity and latent heat of vaporizations are desirable properties for effective cooling and heating with a small temperature rise during compression [97–99]. Pressure ratio should be small for higher isentropic and volumetric efficiency, and the refrigerant must be miscible with oil for piston lubrication. The low specific volume at the suction of compressor indicates the lower size of compressor [44,100,101]. Domanski et al. [40] identified T_{Critc}, p_{Crict}, $C^{\circ}p$, ω as the most influencing parameters and their optimal values for

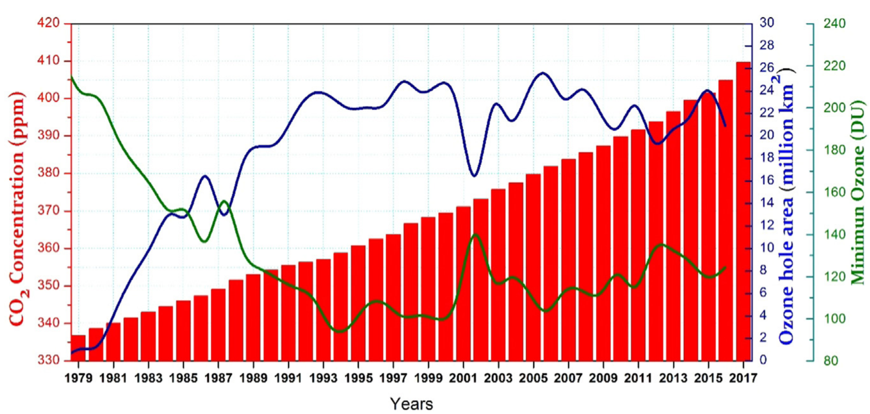


Fig. 6. Ozone hole area and minimum ozone level plot [81,82].

Fig. 7. Normalization of optimal properties of refrigerants.

the performance limit for VCC. An ideal refrigerant should be non-flammable and non-toxic in accordance with ASHREA/ANSI 34 Standard.

Several refrigerants screenings and optimization studies are available focusing thermo-physical, heat transfer environmental and economic aspects. Saleh and Wendland [15] proposed physical BACKBONE equation; Kucuksille et al. [102] suggested data mining technique by using WEKA software. Other studies on the topic include neural networks [103], hybrid formulae for thermodynamic properties [104], cost based methods [105], entrainment ratio techniques [106], and comparison of operating performance [3]. Commercially available software for thermo-physical properties of fluids includes REFPROP, Solkane, Propath, X Props but the quest of an easy way out to replace the discarded refrigerants in phase with global requirements remains a quandary that how to choose the correct refrigerant for the right application. Industrialists do not trust local suppliers for their business interests. Users need a comprehensive optimization method to decide the replacement of refrigerants owing existing ozone depletion and global warming, without compromising efficiency, for their long term financial benefits. This is the point we have taken into account to suggest the qualitative parametric estimation model as we have described in authors preceding work [107] under which users can normalize the parameters from 1 to 0 by dividing the actual values with the highest in the list. They can normalize the unfavorable values by dividing with the largest ones that is followed by subtracting out the largest value. The division will normalize the values and subtraction in the case of uncomplimentary values will assign them appropriate values varying between certain ranges for all refrigerants.

For instance, the heat of vaporization at evaporation (−15 °C) temperature of R717 is 1312.2 kJ/kg as compared to 209.5 kJ/kg of R-134a, which will become 1 and 0.16 after the normalization division with 1312.2. After calculating normalized values and keeping in mind the major techno-economic and environmental parameters, we can multiply the columns with suitable normalization curve if necessary. Finally, the refrigerant choice optimization can be obtained by dividing the actual technical and environmental parametric values through the sum of ideal optimum values. The refrigerant parametric quantification (RPQ) may be obtained by the summation sum of environmental (env), physical (phys), transport (trans); performance (perf), chemical (chem) and economic (eco) parameters, varying from i to n and o to t numbers.

$$RPQ = \frac{\sum_i^o P_{env}^i + \sum_j^p P_{phys}^j + \sum_k^q P_{trans}^k + \sum_l^r P_{perf}^l + \sum_m^s P_{chem}^m + \sum_n^t P_{eco}^n}{o+p+q+r+s+t} \times 100 \tag{7}$$

The quality quantification of environmental, physical, trans-critical, performance, chemical and economic parameters may be given as:

$$\sum_i^m P_{env}^i = A_{ODP}^1 + B_{GWP}^2 + C_{Life}^3 + D_{MROA}^4 + \ldots\ldots \tag{8}$$

$$\sum_j^p P_{phys}^j = T_{FP}^1 + P_{NBP}^2 + T_{CP}^3 + T_{IG}^4 + p_{critc}^5 + h_{fg-evapo}^6 + V_{sp}^7 + \ldots \tag{9}$$

$$\sum_k^q P_{trans}^k = \mu_l^1 + \mu_v^2 + \kappa_l^3 + \kappa_v^4 + h_{fg-conds}^5 + \sigma_l^6 + \sigma_v^7 + p_{reduc}^8 + \ldots \tag{10}$$

$$\sum_l^r P_{perf}^l = +C^\circ p_{298K}^1 + M^2 + CR^3 + \omega^4 + \ldots \tag{11}$$

$$\sum_m^s P_{Chem}^m = L_{ASHREA-34}^1 + M_{\mathrm{Re}\,activity}^2 + \ldots \tag{12}$$

$$\sum_n^t P_{Eco}^m = G_{Cost}^1 + H_{Availibility}^2 + \ldots \tag{13}$$

The sum of o, p, q to r depends on a number of parameters evaluated for optimization. To account for the essential parameters, the array of normalized discrete fractional values between 1 and 0 may further be convoluted with any significant comb function that can be more practical on choice rather than relying on basic optimization hallucinations. This multiplier function may be distinct for environmental, physical, trans-critical, performance, chemical and economic values as well as for the global priorities like the environment or technical limitations to stay in phase with nature. A priority distribution function assuming quality factor QC may be given as:

$$P = \frac{1}{2\pi} e^{-Q_C^2/2} \tag{14}$$

Parameter QC may be chosen for its maximum value of unity akin to normal distribution function. A graphical illustration of multiplying sampled normalized values with priority function is illustrated in Fig. 7.

Environmental, physical, trans-critical, performance, chemical and economic quality factors may be separately multiplied in their own groups before final combined multiplication. The central QC parameter allows normal distribution profiles, assuming LHS parameters, bearing negative signs like normal probability functions spanning around the x-axis. The parametric optimization method is akin to determine the democratic election of most eligible candidates.

To test the above optimization procedure, a standard VCC (−15 °C to +30 °C) is chosen to apply ASHREA typical cycle conditions as shown in Fig. 8 [108]. The cycle variations may change the choice of optimal refrigerants due to inherent thermo-physical and transport properties. The number of parameters may be increased or decreased

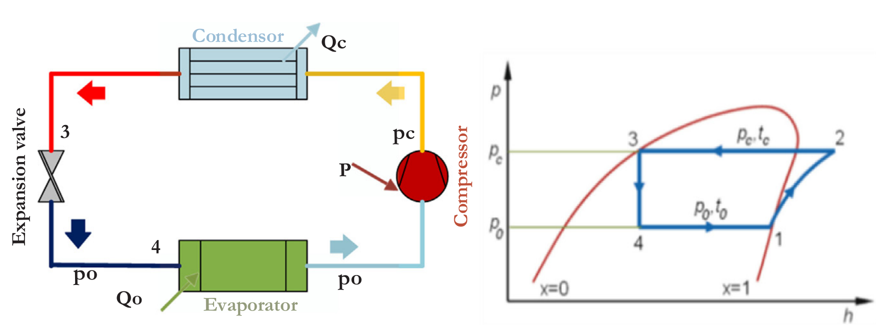


Fig. 8. Standard Vapour Compression Cycle (VCC) along its p-h diagram.

based upon system requirements; however, in the present work, 25 the most influencing parameters are chosen based [17,38,40] on the performance of refrigeration and heat pump systems as suggested by various authors from open literature.

Thermo-physical properties are computed by REFPROP, a standard software by The National Institute of Standards and Technology (NIST) [109] whereas, flammability classification is adopted from ASHREA Standard 34 [42]. Chemical reactivity, cost, and availability parameters are computed from open literature, local and international market.

For typical VCC, the refrigerants should have a minimum pressure drop, which can be achieved through thermo-physical characteristics like the lower viscosity, high density, and heat of vaporization [94]. According to cooper's pool boiling correlation [95], the refrigerants offering higher reduced pressure and lower molecular weight result in high heat transfer in boiling [96]. However, at condensation, high density, thermal conductivity and latent heat of vaporizations are desirable properties for efficient cooling and heating with a small temperature rise during compression. Pressure ratio should be low for higher isentropic and volumetric efficiency and the refrigerant must be miscible with oil for piston lubrication [20]. The low specific volume at the suction of compressor indicates the smaller size of compressor [101]. Domanski et al. identified $T_{Critc,}$ p_{Crict}, $C^{\circ}p$, ω as the most influencing parameters and their optimal values for the performance limit for VCC. An ideal refrigerant should be non-flammable and non-toxic in agreement with ASHREA/ANSI 34 standard [40].

Refrigerants parameters described in Tables 1 and 2 are chosen very carefully. The environmental category is interconnected recommendations of Montreal-Kyoto protocols, F-Gas law and Paris Agreement and their time to time amendments. Refrigerant parameters described in Table 1 and Table 2 are normalized by the optimal ranges defined in Table 4, and the results of ASHREA standard vapour compression cycle (VCC) are shown in Fig. 8(a-d).

Environmental quality parameters of selected refrigerants were normalized to assign the fractional weight. Natural refrigerants (R-744, R-717), environmentally benign, result in highest quality weight when accounted for ODP, GWP and life in the atmosphere; some newly developed HFO's (R-1234yf, R-1234ze) have good aggregate as compared to existing synthetic refrigerants (CFC, HFC, HCFC) as shown in Fig. 9(a). Synthetic refrigerants owing to high GWP and long atmospheric life as compared to CO_2 are not environmentally favorable and on the way to phase out.

Refereeing to Fig. 9(b), physical properties of synthetic refrigerants as a viewpoint, HFOs and some HCs (R-600, R-600a, R-1270) have almost a similar quality weight. CFC 12 and HCFC 22 have an aggregated average above 51%. From Fig. 9(b), it is evident that R-744, R-717, and R-170 have arisen as prominent refrigerants with leading quality weight with respect to the thermodynamic space of physical properties.

From Fig. 9(c), it is evident that R-744, R-717, and R-170 have arisen as prominent refrigerants with leading quality weight, on the thermodynamic space of physical properties for standard VCC (−15 °C to 30 °C). However, when the temperature of the condenser or evaporator changes as per regional requirements like in Pakistan, where the ambient temperature in the summer remains in 40–50 °C, the choice of refrigerants will be changed accordingly.

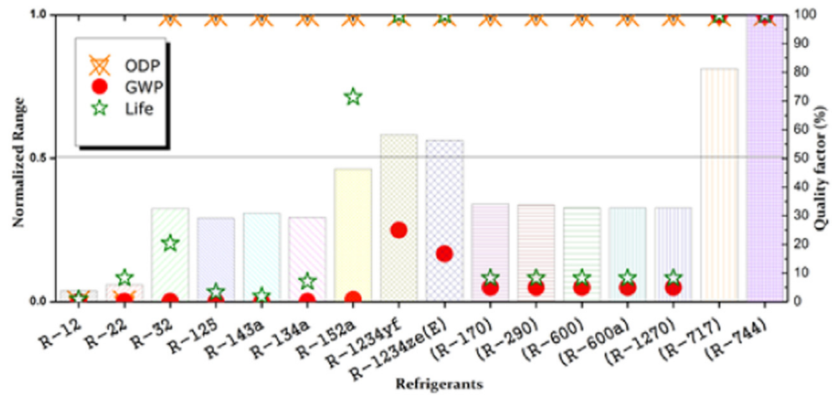
Fig. 9(d) shows normalized values of chemical, fiscal and performance properties along with quality factor. In this window, Synthetic refrigerants (CFC, HCFC, and HFC) have higher weighted quality factor than HFO's. R-717 and R-1270 carry nearly equal weight. Once again Carbon dioxide (R-744) has a higher quality factor (83%), while R-170 (77%), R-290 (66%) have significant weight.

The results of the proposed RPQ method are also supported by experimental test results reported in the literature, a comparison study of between R-134a and R-1234yf [39], R-12 and R-290 [15], R-22, R-290 [1], R-1234yf, R-134a, R-290 [65], R-717, R-744, R-134a, R-12, R-22 [7], R-290, R-600, R-600a, R-1270, R-22 [14,16,20], R-12, R-134a, R-290 [3], R-744, R-717, R-290, R-1234yf [111] and author's own previous simulation results among R-170, R-290, R-600, R-600a, R-717 [37].

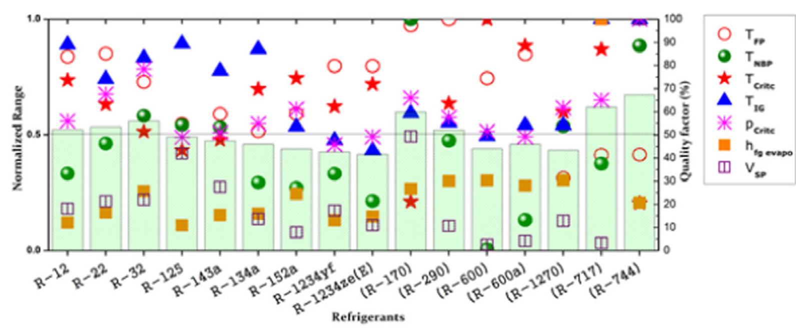
Carbon dioxide (R-744) is revitalizing as an optimum refrigerant for heating, air-conditioning, and refrigeration applications. Various renowned researchers suggest the use of CO_2 in solar powered air-conditioning, heating, Single and multi-stage VCC, multistage saturation [61,66] and heating in sub zero temperature areas [36]. CO_2 (R-744) has replaced glycols, and salt brines as a secondary refrigerant [67]. German and Japanese auto industries have chosen CO_2 for their next generation mobile air conditioners. Japan has already started the

Table 4
Normalized parameters of techno-economic parameters [2,9,96,110].

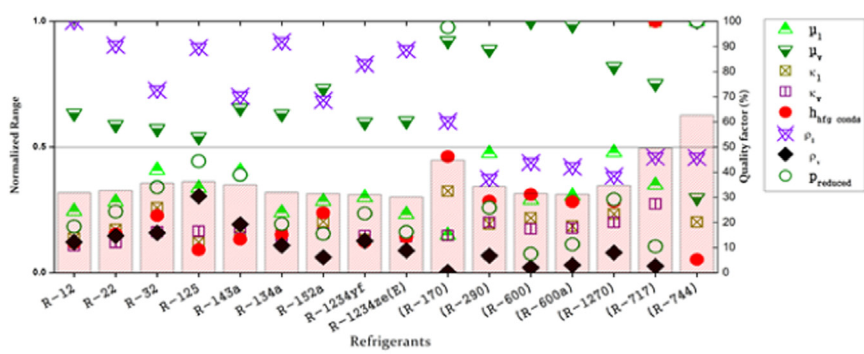
Normalized Parameter	Optimal value / Normalized value
ODP_n	1 (zero ODP), 0 (having ODP) [81]
GWP_n	= $1/GWP_a$ (Normalized to GWP of CO_2) [81]
$Life_n$	= $0.019/Life_a$(Normalized to life of R-717 being the lowest).
$MROA_n$	= $MROA_a$/1726.9 °C (Normalized by maximum operational temperature of R-744).
$T_{FP\text{-}n}$	= $T_{FP\text{-}a}$/ − 188 °C (Normalized by lowest freezing temperature of R-290) [100]
$T_{NBP\text{-}n}$	= $T_{NBP\text{-}a}$ / − 88.58 °C (Normalized by lowest normal boiling temperature of R-170)[100]
$T_{CP\text{-}n}$	= T_{CPa} / 151.98 (Normalized by highest critical temperature of R-600 among chosen refrigerants) [40]
$T_{IG\text{-}n}$	= $T_{IG\text{-}a}$ / 850 (Normalized by higher ignition temperature of R-717; whilst R-744 = 1.0 due to non-flammability [4,83,44].
$P_{crit\text{-}n}$	= $P_{crit\text{-}a}$/73.3 (Normalized by critical temperature of R-744, for refrigerants having P_{crit} > 73.3 the normalization leads to = 73.3/ $P_{crit\text{-}a}$) [40]
$h_{fgevap\text{-}n}$	= $h_{fgevap\text{-}a}$/1313.2 (Normalized by highest value latent heat of vaporization of R-717)[100]
$V_{SP\ evap\text{-}n}$	= 0.01646/$V_{SP\ evap\text{-}a}$ (Normalized to lowest specific volume at an evaporator temp. of R- 744)
$\mu_{l\text{-}n}$	= 43.76/ $\mu_{l\text{-}a}$ (Normalized to lowest liquid dynamic viscosity at T_{conds}(R-744) [20]
$\mu_{v\text{-}n}$	= 7.51/ $\mu_{v\text{-}a}$ (Normalized to lowest vapor dynamic viscosity at T_{conds} (R-744) [20]
$k_{l\text{-}n}$	= $k_{l\text{-}a}$ /471.35 (Normalized by maximum liquid thermal conductivity at T_{conds} (R-717) [20]
$k_{v\text{-}n}$	= $k_{v\text{-}a}$ /98.02 (Normalized by maximum liquid thermal conductivity at T_{conds} (R-747) [20]
$h_{fg\text{-}n}$	= $h_{fg\text{-}a}$/1144.4 (Normalized by maximum heat of vaporization at T_{conds} (R-717) [20]
$\rho_{l\text{-}n}$	= $\rho_{l\text{-}a}$ /1292.7 (Normalized by maximum liquid density of R-717 at T_{conds}) [20]
$\rho_{v\text{-}n}$	= $\rho_{v\text{-}a}$/345.1 (Normalized by maximum liquid density of R−-747 at T_{conds}) [20]
$p_{reduc\text{-}n}$	= $p_{reduc\text{-}a}$ /0.978 (Normalized by highest reduced pressure exhibited by R-744) [95]
$C^{\circ}_{p\text{-}n}$	= 35.637/$C^{\circ}_{p\text{-}a}$(Normalized to specific heat of R-717 being optimum for simple VCC) [40]
M_n	= 17.03/M_a (Normalized to lowest molecular weight exhibited by R-717) [66]
CR_n	= 2.85/CR_n(Normalized to lowest compression ratio of R-170 [101]
ω_n	= 0.0995/ ω_a(Normalized to lowest value of R-170 [40]
L_n	(Toxicity (0.5) + Flammability (0.5) A1 = 1, A2L= 0.87, A2 = 0.75, A3 = 0.5, B1 = 0.5, B2L= 0.37, B2 = 0.25, B3 = 0 [9]
M_n	1 (Non-corrosive), 0.5 (corrosive with copper or Steel), 0 (Corrosive with copper & steel).
G_n	= 0.7 $-kg/$G_a$(Normalized to lowest cost of R-744).
H_n	1 (Available), 0 (Not available).



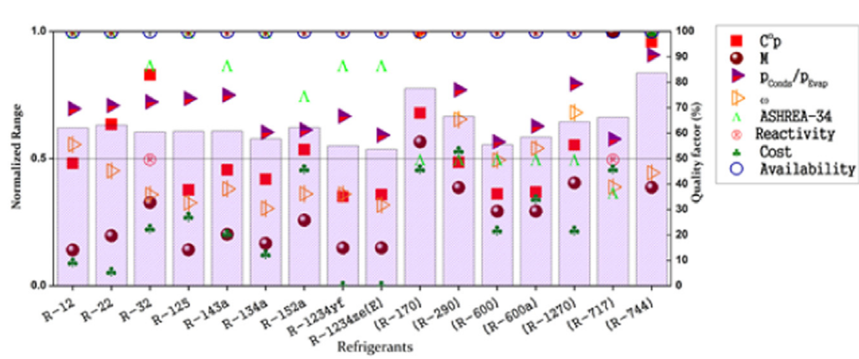
(a) Environmental properties of refrigerants.



(b) Physical properties of refrigerants.



(c) Transport properties of refrigerants.



(d) Performance, chemical and fiscal properties of refrigerants.

Fig. 9. Refrigerant parameters normalized from 0.0 (low) to 1.0 (high).

production of the water heater (EcoCute) by using CO_2 as working fluid. In synthetic refrigerants, newly developed HFOs (R-1234yf) and low GWP HFC 152a have favorable quality weight and seem potential candidates for next generation heat pump applications.

6. Conclusions

This paper reviews past, present and future outlook of natural and synthetic refrigerants under Kyoto and Montreal Protocols, F-gas law and Paris Accord. Most of the extant synthetic refrigerants (HFC and HCFC) do not qualify the environmental benign meritorious barriers and will be phased out. We are fast approaching the deadline (2020–2030), yet many countries are uncertain or unaware. Time-barred permission to continue the use of HFCs is an interim solution, not a justification. This work has presented a model of parametric quantification of natural and synthetic refrigerants to optimize the decision process. Parametric quantification gives a better choice by using techno-economic data of refrigerants. In present study CO_2 (R-744), Ammonia (R-717) and Ethane (R-170) are concluded to be superior options among ASHREA envisaged natural refrigerants. Synthetic refrigerants like R-152a, R-1234yf, and R-1234ze have equal rather better performance than R-717 and R-170 refrigerants. However, the flammability and safety are still potential challenges in using hydrocarbonrefrigerants in heat pump systems. Several synthetic refrigerants have comparatively good quality weights, yet are overlooked due to environmental constraints. This paper facilitates the optimal choice of refrigerants for industries, willing to make timely transfers from CFCs to HCFC, HCFC to HFC or HFO and HFC or HFO to natural refrigerants in compliance with global responsibilities.

Acknowledgements

This research was supported by a grant from the Pakistan-US Science and Technology Cooperation Program (Project ID No. 299), US Department of State (jointly administered by the National Academics and Higher Education Commission of Pakistan).

References

[1] Riffat SB, Afonso CF, Oliveira AC, Reay DA. Natural refrigerants for refrigeration and air-conditioning systems. Appl Therm Eng 1997;17:33–42. http://dx.doi.org/10.1016/1359-4311(96)00030-0.
[2] Calm JM. The next generation of refrigerants – Historical review, considerations, and outlook. Int J Refrig 2008;31:1123–33. http://dx.doi.org/10.1016/j.ijrefrig.2008.01.013.
[3] Halimic E, Ross D, Agnew B, Anderson A, Potts I. A comparison of the operating performance of alternative refrigerants. Appl Therm Eng 2003;23:1441–51. http://dx.doi.org/10.1016/S1359-4311(03)00081-4.
[4] Benhadid-Dib S, Benzaoui A. Refrigerants and their environmental impact substitution of hydro chlorofluorocarbon HCFC and HFC hydro fluorocarbon. Search for an adequate refrigerant. Energy Proc 2012;18:807–16. http://dx.doi.org/10.1016/j.egypro.2012.05.096.
[5] Ciconkov R. Refrigerants: there is still no vision for sustainable solutions. Int J Refrig 2018;86:441–8. http://dx.doi.org/10.1016/j.ijrefrig.2017.12.006.
[6] Calm JM. The next generation of refrigerants - Historical review, considerations, and outlook. Int J Refrig 2008;31:1123–33. http://dx.doi.org/10.1016/j.ijrefrig.2008.01.013.
[7] Lorentzen G. Revival of carbon dioxide as a refrigerant. Int J Refrig 1994;17:292–301. http://dx.doi.org/10.1016/0140-7007(94)90059-0.
[8] Wang J, Zhao P, Niu X, Dai Y. Parametric analysis of a new combined cooling, heating and power system with transcritical CO_2 driven by solar energy. Appl Energy 2012;94:58–64. http://dx.doi.org/10.1016/j.apenergy.2012.01.007.
[9] Abas N, Nawaz R, Khan N. Parametric quantification of low GWP refrigerant for thermosyphon driven solar water heating system. Proc Comput Sci 2015;52:804–11. http://dx.doi.org/10.1016/j.procs.2015.05.136.
[10] Li Q, Piechna J, Müller N. Thermodynamic potential of using a counter rotating novel axial impeller to compress water vapor as refrigerant. Int J Refrig 2011;34:1286–95. http://dx.doi.org/10.1016/j.ijrefrig.2011.03.002.
[11] Calm JM. The next generation of refrigerants? Historical review, considerations, and outlook. Int J Refrig 2008;31:1123–33. http://dx.doi.org/10.1016/j.ijrefrig.2008.01.013.
[12] Kilicarslan A, Müller N. A comparative study of water as a refrigerant with some current refrigerants. Int J Energy Res 2005;29:947–59. http://dx.doi.org/10.1002/er.1084.
[13] Lachner BF, Nellis GF, Reindl DT. The commercial feasibility of the use of water vapor as a refrigerant. Int J Refrig 2007;30:699–708. http://dx.doi.org/10.1016/j.ijrefrig.2006.09.009.
[14] Granryd E. Hydrocarbons as refrigerants — an overview. Int J Refrig 2001;24:15–24. http://dx.doi.org/10.1016/S0140-7007(00)00065-7.
[15] Saleh B, Wendland M. Screening of pure fluids as alternative refrigerants. Int J Refrig 2006;29:260–9. http://dx.doi.org/10.1016/j.ijrefrig.2005.05.009.
[16] Chang Y, Kim M, Ro S. Performance and heat transfer characteristics of hydrocarbon refrigerants in a heat pump system. Int J Refrig 2000;23:232–42. http://dx.doi.org/10.1016/S0140-7007(99)00042-0.
[17] Lemmon EW, Huber ML, Mclinden MO NIST Reference Fluid Thermodynamic and Transport Properties — REFPROP n.d.
[18] Robinson C, Smith DB. The auto-ignition temperature of methane. J Hazard Mater 1984;8:199–203. http://dx.doi.org/10.1016/0304-3894(84)85001-3.
[19] James R, Missenden J. The use of propane in domestic refrigerators. Int J Refrig 1992;15:95–100. http://dx.doi.org/10.1016/0140-7007(92)90033-Q.
[20] Palm B. Hydrocarbons as refrigerants in small heat pump and refrigeration systems – A review. Int J Refrig 2008;31:552–63. http://dx.doi.org/10.1016/j.ijrefrig.2007.11.016.
[21] UNEP. Report of the refrigeration, air conditioning and heat pumps technical options committee; 2014.
[22] Bolaji BO, Huan Z. Ozone depletion and global warming: case for the use of natural refrigerant – a review. Renew Sustain Energy Rev 2013;18:49–54. http://dx.doi.org/10.1016/j.rser.2012.10.008.
[23] Jwo C-S, Ting C-C, Wang W-R. Efficiency analysis of home refrigerators by replacing hydrocarbon refrigerants. Measurement 2009;42:697–701. http://dx.doi.org/10.1016/j.measurement.2008.11.006.
[24] Kinsell RC, Noe JC, Byrne JP. Air Cycle air conditioning system for vehicles. US1977/4015438; 1977.
[25] Makyea. Air to air refrigeration; 2014.
[26] Miller JP, Smith CD, Allam RJ, Topham JAK. Refrigeration system; 1996.
[27] Park SK, Ahn JH, Kim TS. Off-design operating characteristics of an open-cycle air refrigeration system. Int J Refrig 2012;35:2311–20. http://dx.doi.org/10.1016/j.ijrefrig.2012.08.005.
[28] Pearson A. Refrigeration with ammonia. Int J Refrig 2008;31:545–51. http://dx.doi.org/10.1016/j.ijrefrig.2007.11.011.
[29] Palm B. Ammonia in low capacity refrigeration and heat pump systems. Int J Refrig 2008;31:709–15. http://dx.doi.org/10.1016/j.ijrefrig.2007.12.006.
[30] Didion D, Brown JS. Challenges in Developing Environmentally Safe Heat Pumping Systems. ASME-ZSITS Int. Therm. Sci. Semin., Bled; 2000.
[31] Zhong Y, Critoph RE, Thorpe R. Evaluation of the performance of solid sorption refrigeration systems using carbon dioxide as refrigerant. Appl Therm Eng 2006;26:1807–11. http://dx.doi.org/10.1016/j.applthermaleng.2006.02.006.
[32] Lorentzen G, Pettersen J, Bang RR. Method of high-side pressure regulation in transcritical vapor compression cycle device; 1993.
[33] Abas N, Khan N, Hussain I. A Solar Water Heater for Subzero Temperature Areas. Prog. Sustain. Energy Technol. Gener. Renew. Energy, Cham: Springer International Publishing; 2014, p. 369–77. 〈https://doi.org/10.1007/978-3-319-07896-0_20〉.
[34] Abas N, Khan N. A thermosyphon driven solar water heater using CO 2 as working fluid. J Appl Environ Biol Sci 2016;6:43–54.
[35] Abas N, Khan N. Theory and design of counter flow shell-and-coil heat exchanger for CO_2 based solar water heater. Int J Therm Environ Eng 2015:10. http://dx.doi.org/10.5383/ijtee.10.02.001.
[36] Abas N, Khan N, Haider A, Saleem MS. A thermosyphon solar water heating system for sub zero temperature areas. Cold Reg Sci Technol 2017;143:81–92. http://dx.doi.org/10.1016/j.coldregions.2017.08.012.
[37] Abas N, Khan N. Carbon conundrum, climate change, CO_2 capture and consumptions. J CO_2 Util 2014;8:39–48. http://dx.doi.org/10.1016/j.jcou.2014.06.005.
[38] McLinden MO, Kazakov AF, Steven Brown J, Domanski PA. A thermodynamic analysis of refrigerants: possibilities and tradeoffs for Low-GWP refrigerants. Int J Refrig 2014;38:80–92. http://dx.doi.org/10.1016/j.ijrefrig.2013.09.032.
[39] Jarahnejad M. New Low GWP Synthetic Refrigerants Low GWP Synthetic Refrigerants. KTH; 2012.
[40] Domanski PA, Steven Brown J, Heo J, Wojtusiak J, McLinden MO. A thermodynamic analysis of refrigerants: performance limits of the vapor compression cycle. Int J Refrig 2014;38:71–9. http://dx.doi.org/10.1016/j.ijrefrig.2013.09.036.
[41] ASHREA. ASHREA position document on Natural Refrigerants; 2011.
[42] ASHREA. ASHREA 34 Standard; 2007.
[43] Abas N, Nawaz R, Khan N. Parametric quantification of low GWP refrigerant for thermosyphon driven solar water heating system. Proc Comput Sci 2015;52:804–11. http://dx.doi.org/10.1016/j.procs.2015.05.136.
[44] Mohanraj M, Jayaraj S, Muraleedharan C. Environment friendly alternatives to halogenated refrigerants—A review. Int J Greenh Gas Control 2009;3:108–19. http://dx.doi.org/10.1016/j.ijggc.2008.07.003.
[45] Mota-Babiloni A, Navarro-Esbrí J, Molés F, Cervera ÁB, Peris B, Verdú G. A review of refrigerant R1234ze(E) recent investigations. Appl Therm Eng 2016;95:211–22. http://dx.doi.org/10.1016/j.applthermaleng.2015.09.055.
[46] Mota-Babiloni A, Makhnatch P, Khodabandeh R. Recent investigations in HFCs substitution with lower GWP synthetic alternatives: focus on energetic performance and environmental impact. Int J Refrig 2017;82:288–301. http://dx.doi.org/10.1016/j.ijrefrig.2017.06.026.
[47] Kopko WL. Beyond CFCs: extending the search for new refrigerants. Int J Refrig 1990;13:79–85. http://dx.doi.org/10.1016/0140-7007(90)90005-H.
[48] Devotta S, Gopichand S. Comparative assessment of HFC134a and some refrigerants as alternatives to CFC12. Int J Refrig 1992;15:112–8. http://dx.doi.org/10.1016/0140-7007(92)90035-S.
[49] Holcomb CD, Niesen VG, Van Poolen LJ, Outcalt SL. Coexisting densities, vapor pressures and critical densities of refrigerants R-32 and R-152a, at 300–385 K.

Fluid Phase Equilib 1993;91:145–57. http://dx.doi.org/10.1016/0378-3812(93)85085-Z.
[50] Niesen VG, Van Poolen LJ, Outcalt SL, Holcomb CD. Coexisting densities and vapor pressures of refrigerants R-22, R-134a, and R-124 at 300?395 K. Fluid Phase Equilib 1994;97:81–95. http://dx.doi.org/10.1016/0378-3812(94)85008-9.
[51] Lorentzen G. The use of natural refrigerants: a complete solution to the CFC/HCFC predicament. Int J Refrig 1995;18:190–7. http://dx.doi.org/10.1016/0140-7007(94)00001-E.
[52] Lisal M, Vacek V. Effective potentials for liquid simulation of the alternative refrigerants HFC-32: CH2F2 and HFC-23: CHF3. Fluid Phase Equilib 1996;118:61–76. http://dx.doi.org/10.1016/0378-3812(95)02848-X.
[53] Barley MH, Morrison JD, O'Donnel A, Parker IB, Petherbridge S, Wheelhouse RW. Vapour-liquid equilibrium data for binary mixtures of some new refrigerants. Fluid Phase Equilib 1997;140:183–206. http://dx.doi.org/10.1016/S0378-3812(97)00146-5.
[54] Calero S, Wendland M, Fischer J. Description of alternative refrigerants with BACKONE equations. Fluid Phase Equilib 1998;152:1–22. http://dx.doi.org/10.1016/S0378-3812(98)00376-8.
[55] Hammad M, Alsaad M. The use of hydrocarbon mixtures as refrigerants in domestic refrigerators. Appl Therm Eng 1999;19:1181–9. http://dx.doi.org/10.1016/S1359-4311(98)00116-1.
[56] Stegou-Sagia A, Damanakis M. Binary and ternary blends of R-134a as alternative refrigerants to R-22. Energy Convers Manag 2000;41:1345–59. http://dx.doi.org/10.1016/S0196-8904(99)00191-0.
[57] Wongwises S, Pirompak W. Flow characteristics of pure refrigerants and refrigerant mixtures in adiabatic capillary tubes. Appl Therm Eng 2001;21:845–61. http://dx.doi.org/10.1016/S1359-4311(00)00090-9.
[58] Xuan Y, Chen G. Experimental study on HFC-161 mixture as an alternative refrigerant to R502. Int J Refrig 2005;28:436–41. http://dx.doi.org/10.1016/j.ijrefrig.2004.04.003.
[59] Park K-J, Jung D. Thermodynamic performance of HCFC22 alternative refrigerants for residential air-conditioning applications. Energy Build 2007;39:675–80. http://dx.doi.org/10.1016/j.enbuild.2006.10.003.
[60] Park K-J, Jung D. Performance of alternative refrigerant R430A on domestic water purifiers. Energy Convers Manag 2009;50:3045–50. http://dx.doi.org/10.1016/j.enconman.2009.07.024.
[61] Bolaji BO. Performance investigation of ozone-friendly R404A and R507 refrigerants as alternatives to R22 in a window air-conditioner. Energy Build 2011;43:3139–43. http://dx.doi.org/10.1016/j.enbuild.2011.08.011.
[62] Wallington TJ, Andersen MPS, Nielsen OJ. Atmospheric chemistry of short-chain haloolefins: photochemical ozone creation potentials (POCPs), global warming potentials (GWPs), and ozone depletion potentials (ODPs). Chemosphere 2015;129:135–41. http://dx.doi.org/10.1016/j.chemosphere.2014.06.092.
[63] Antunes AHP, Bandarra Filho EP. Experimental investigation on the performance and global environmental impact of a refrigeration system retrofitted with alternative refrigerants. Int J Refrig 2016;70:119–27. http://dx.doi.org/10.1016/j.ijrefrig.2016.06.027.
[64] Harby K. Hydrocarbons and their mixtures as alternatives to environmental unfriendly halogenated refrigerants: an updated overview. Renew Sustain Energy Rev 2017;73:1247–64. http://dx.doi.org/10.1016/j.rser.2017.02.039.
[65] Navarro E, Martínez-Galvan IO, Nohales J, Gonzálvez-Maciá J. Comparative experimental study of an open piston compressor working with R-1234yf, R-134a and R-290. Int J Refrig 2013;36:768–75. http://dx.doi.org/10.1016/j.ijrefrig.2012.11.017.
[66] Palm B. Ammonia in low capacity refrigeration and heat pump systems. Int J Refrig 2008;31:709–15. http://dx.doi.org/10.1016/j.ijrefrig.2007.12.006.
[67] Arrhenius S. in the Air upon the Temperature of the Ground. Philos Mag J Sci 1896;41:237–79.
[68] Molina MJ, Rowland FS. Stratospheric sink for chlorofluoromethanes: chlorine atomc-atalysed destruction of ozone. Nature 1974;249:810–2. http://dx.doi.org/10.1038/249810a0.
[69] Douglas L. Global warming. New Delhi: Viva Books Private Limited; 2005.
[70] Ma Y, Ma W, Zhong L, Hu Z, Li M, Zhu Z, et al. Monitoring and Modeling the Tibetan Plateau's climate system and its impact on East Asia. Sci Rep 2017;7:44574. http://dx.doi.org/10.1038/srep44574.
[71] Ko MKW, Sze ND, Molnar G, Prather MJ. Global warming from chlorofluorocarbons and their alternatives: time scales of chemistry and climate. Atmos Environ Part A Gen Top 1993;27:581–7. http://dx.doi.org/10.1016/0960-1686(93)90215-K.
[72] Nations U. The Montreal Protocol on Substances that Deplete the Ozone Layer; 1997.
[73] UN. Kyoto Protocol. United Nations Fram Work Conv Clim Chang; 2012. 〈http://unfccc.int/kyoto_protocol/items/2830.php〉.
[74] US EPA. Health and Environmental Effects of Ozone Layer Depletion. US EPA Website. 〈https://www.epa.gov/ozone-layer-protection/health-and-environmental-effects-ozone-layer-depletion〉 [Accessed 15 June 2017]; 2017.
[75] Sekiya A. The evaluation of time variation global warming effects, TWPA and CWP, for CFC alternatives. J Fluor Chem 2007;128:1137–42. http://dx.doi.org/10.1016/j.jfluchem.2007.04.024.
[76] Dalmasso PR, Taccone RA, Nieto JD, Cometto PM, Lane SI. Hydrochloroethers in the troposphere: kinetics with Cl atoms, lifetimes and atmospheric acceptability indices. Atmos Environ 2012;47:104–10. http://dx.doi.org/10.1016/j.atmosenv.2011.11.028.
[77] IPCC. IPCC Fourth Assessment Report: Climate Change; 2007.
[78] McLinden MO, Kazakov AF, Steven Brown J, Domanski PA. A thermodynamic analysis of refrigerants: possibilities and tradeoffs for Low-GWP refrigerants. Int J Refrig 2014;38:80–92. http://dx.doi.org/10.1016/j.ijrefrig.2013.09.032.
[79] Abas N, Kalair A, Khan N, Kalair AR. Review of GHG emissions in Pakistan compared to SAARC countries. Renew Sustain Energy Rev 2017;80:990–1016. http://dx.doi.org/10.1016/j.rser.2017.04.022.
[80] US Department of Commerce. NOAA ESRL. ESRL Global Monitoring Division - Global Greenhouse Gas Reference Network. 〈https://www.esrl.noaa.gov/gmd/ccgg/trends/〉. [Accessed 11 June 2017]; 2017.
[81] EPA. Ozone Layer Protection Share; 2016.
[82] NOAA. CO2 monitoring records. Mauna Loa Lab Rep; 2016. 〈http://www.esrl.noaa.gov/gmd/ccgg/trends〉.
[83] Yang Z, Wu X. Retrofits and options for the alternatives to HCFC-22. Energy 2013;59:1–21. http://dx.doi.org/10.1016/j.energy.2013.05.065.
[84] Keller CA, Hill M, Vollmer MK, Henne S, Brunner D, Reimann S, et al. European emissions of halogenated greenhouse gases inferred from atmospheric measurements. Environ Sci Technol 2012;46:217–25. http://dx.doi.org/10.1021/es202453j.
[85] IPCC. Projections of Future Changes in Climate - AR4 WGI Summary for Policymakers. IPCC Fourth Assess Rep Clim Chang n.d. 〈https://www.ipcc.ch/publications_and_data/ar4/wg1/en/spmsspm-projections-of.html〉. [Accessed 7 June 2017]; 2007.
[86] IPCC. Projections of Future Changes in Climate; 2007.
[87] NOAA NASA, UNEP WMO. EC. Scientific a Ssessment of O Zone D Epletion; 2014.
[88] Abas N, Kalair A, Khan N. Review of fossil fuels and future energy technologies. Futures 2015;69:31–49. http://dx.doi.org/10.1016/j.futures.2015.03.003.
[89] Khan N, Abas N, Mariun N. IMPACT OF GLOBAL WARMING ON TREES. Glob. Conf. Glob. Warm; 2008.
[90] Allouhi A, Kousksou T, Jamil A, Bruel P, Mourad Y, Zeraouli Y. Solar driven cooling systems: an updated review. Renew Sustain Energy Rev 2015;44:159–81. http://dx.doi.org/10.1016/j.rser.2014.12.014.
[91] Averfalk H, Ingvarsson P, Persson U, Gong M, Werner S. Large heat pumps in Swedish district heating systems. Renew Sustain Energy Rev 2017;79:1275–84. http://dx.doi.org/10.1016/j.rser.2017.05.135.
[92] Rad FM, Fung AS. Solar community heating and cooling system with borehole thermal energy storage – Review of systems. Renew Sustain Energy Rev 2016;60:1550–61. http://dx.doi.org/10.1016/j.rser.2016.03.025.
[93] Azmi WH, Sharif MZ, Yusof TM, Mamat R, Redhwan AAM. Potential of nanorefrigerant and nanolubricant on energy saving in refrigeration system – A review. Renew Sustain Energy Rev 2017;69:415–28. http://dx.doi.org/10.1016/j.rser.2016.11.207.
[94] Del Col D, Bortolato M, Azzolin M, Bortolin S. Condensation heat transfer and two-phase frictional pressure drop in a single minichannel with R1234ze(E) and other refrigerants. Int J Refrig 2015;50:87–103. http://dx.doi.org/10.1016/j.ijrefrig.2014.10.022.
[95] Cooper MG. Heat Flow Rates in Saturated Nucleate Pool Boiling-A Wide-Ranging Examination Using Reduced Properties, 1984, p. 157–239. 〈http://dx.doi.org/10.1016/S0065-2717(08)70205-3〉.
[96] Gorenflo D, Chandra U, Kotthoff S, Luke A. Influence of thermophysical properties on pool boiling heat transfer of refrigerants. Int J Refrig 2004;27:492–502. http://dx.doi.org/10.1016/j.ijrefrig.2004.03.004.
[97] Slegers L, Seban RA. Nusselt condensation of n-butyl alcohol. Int J Heat Mass Transf 1969;12:237–9. http://dx.doi.org/10.1016/0017-9310(69)90066-0.
[98] Sarkar J. Ejector enhanced vapor compression refrigeration and heat pump systems—A review. Renew Sustain Energy Rev 2012;16:6647–59. http://dx.doi.org/10.1016/j.rser.2012.08.007.
[99] Abdulateef JM, Sopian K, Alghoul MA, Sulaiman MY. Review on solar-driven ejector refrigeration technologies. Renew Sustain Energy Rev 2009;13:1338–49. http://dx.doi.org/10.1016/j.rser.2008.08.012.
[100] Khurmi RS, Gupta JK. Textbook of refrigeration and air conditioning. New Delhi: Eurasia Publishing House; 2011.
[101] Arora C. Refrigeration and air conditioning. New Delhi: Tata McGraw Hill publishing limited; 2000.
[102] Küçüksille EU, Selbaş R, Şencan A. Data mining techniques for thermophysical properties of refrigerants. Energy Convers Manag 2009;50:399–412. http://dx.doi.org/10.1016/j.enconman.2008.09.002.
[103] Şencan A, Kalogirou SA. A new approach using artificial neural networks for determination of the thermodynamic properties of fluid couples. Energy Convers Manag 2005;46:2405–18. http://dx.doi.org/10.1016/j.enconman.2004.11.007.
[104] Sieres J, Varas F, Martínez-Suárez JA. A hybrid formulation for fast explicit calculation of thermodynamic properties of refrigerants. Int J Refrig 2012;35:1021–34. http://dx.doi.org/10.1016/j.ijrefrig.2012.02.008.
[105] Douglas JD, Braun JE, Groll EA, Tree DR. A cost-based method for comparing alternative refrigerants applied to R-22 systems. Int J Refrig 1999;22:107–25. http://dx.doi.org/10.1016/S0140-7007(98)00045-0.
[106] Zheng H, Liang Y, Huang L. Analysis of entrainment ratio about solar ejector refrigerant system. Energy Proc 2012;16:516–21. http://dx.doi.org/10.1016/j.egypro.2012.01.083.
[107] Khan N, Abas N. Comparative study of energy saving light sources. Renew Sustain Energy Rev 2011;15:296–309. http://dx.doi.org/10.1016/j.rser.2010.07.072.
[108] Sarbu I. A review on substitution strategy of non-ecological refrigerants from vapour compression-based refrigeration, air-conditioning and heat pump systems. Int J Refrig 2014;46:123–41. http://dx.doi.org/10.1016/j.ijrefrig.2014.04.023.
[109] Lemmon EW, Huber ML, Mclinden MO. NIST Standard Reference Database 23, NIST Reference Fluid Thermodynamic and Transport Properties-REFPROP; 2013.
[110] Cecchinato L, Corradi M, Fornasieri E, Zamboni L. Carbon dioxide as refrigerant for tap water heat pumps: a comparison with the traditional solution. Int J Refrig 2005;28:1250–8. http://dx.doi.org/10.1016/j.ijrefrig.2005.05.019.
[111] Wang C-C. System performance of R-1234yf refrigerant in air-conditioning and heat pump system – An overview of current status. Appl Therm Eng 2014;73:1412–20. http://dx.doi.org/10.1016/j.applthermaleng.2014.08.012.